Reprinted from JOURNAL OF MAGNETIC RESONANCE
All Rights Reserved by Academic Press, New York and London

Vol. 5, No. 2, October 1971
Printed in Great Britain

Effect of Pressure on Proton Spin–Lattice Relaxation in Several Concentrated Aqueous Electrolyte Solutions*

YUNKO LEE AND J. JONAS

Department of Chemistry, School of Chemical Sciences,
and Materials Research Laboratory, University of Illinois,
Urbana, Illinois 61801

Received May 21, 1971; accepted May 24, 1971

The pressure dependences of the proton nuclear spin–lattice relaxation times of the water molecules in concentrated 4.5 m aqueous solutions of CsBr, RbBr, KBr, LiCl, $CaCl_2$, and $LaCl_3$ have been measured at 25°C up to 2.5 kbars. The proton spin–lattice relaxation times of the aqueous solutions of the structure breaking electrolytes, CsBr, RbBr, and KBr, are longer than that of pure water and decrease with increasing pressure. For all of these three solutions the pressure dependence of T_1 is very similar; however, under the same pressure and at the same temperature the structure breaking ability of the cations increases as $K^+ < Rb^+ < Cs^+$. In concentrated solutions of LiCl, $CaCl_2$, and $LaCl_3$, the proton spin–lattice relaxation times, which are all shorter than T_1 of pure water at the same temperature, increase first to a maximum and then begin to decrease with increasing pressure. The structure-making ability of the cations increases as $Li^+ < Ca^{++} < La^{+3}$ which is parallel to the increase in charge-to-radius ratio of the cations.

INTRODUCTION

Despite the great interest that studies of aqueous solutions have sustained over man decades (*1–3*), no pressure studies of NMR relaxation of aqueous electrolytic solution have been reported. Benedek and Purcell (*4*) and recently Hertz and Radle (*5*) have measured the effect of pressure on the proton T_1 in water. Electrolytes have been classified into structure makers and structure breakers (*6, 7*). Usually, a clear-cut distinction is found between the influence of electrolytes on the structure of water, depending on the nature of the electrolyte.

NMR relaxation studies enable us to investigate molecular reorientational and translational motions in liquids. The structure-making ions reduce the mobility of water molecules by increasing the amount of structure in the aqueous solution, and, as a result, increase the proton spin–lattice relaxation rate of the water molecules. On the contrary, structure breakers, which decrease the amount of water structure in the solution, enhance the mobility of the water molecules and lower the proton relaxation rate as compared to that of pure water. It is known that both temperature and pressure affect the structure of liquids. From the pressure studies on conductance of aqueous

---

* This work was partially supported by the National Science Foundation under Grant GP–12402 and by the Advanced Research Projects Agency under Contract HC–15–67–C–0221.

electrolytic solutions, Horne (*8*), Horne and Johnson (*9*), and Horne and Young (*10*) concluded that pressure is more effective than temperature in destroying water structure.

oth the neutron inelastic scattering investigations of Leung and Safford (*11*) and our unpublished results (*12*) show that at low concentrations the water structure is not strongly disrupted by the electrolytes. Structure makers and structure breakers all behave in a similar way, and properties of the solution remain close to that of pure water. In the present study we investigate only concentrated aqueous electrolytic solutions.

Hertz and Radle (*5*) have found that the proton T_1-vs-pressure dependence of water at 0°C exhibits a maximum. This finding was in agreement with the anomalous pressure dependence of viscosity of water, as the initial application of pressure produces a decrease in viscosity of pure water (*13*) at temperatures below about 30°C. The purpose of this study was to follow the effect of structure-breaking and structure-forming electrolytes on the pressure behavior of the proton spin–lattice relaxation times in several concentrated aqueous electrolyte solutions. Our experimental data have clearly shown the prominent difference in the pressure dependence of T_1 for these two classes of electrolytes.

EXPERIMENTAL

The proton spin–lattice relaxation times were measured at 56.4 MHz using a $180°–\tau–90°$ pulse sequence. The logarithm of the magnetization was plotted as a function of τ to obtain T_1 to $\pm 5\%$. The proton T_1 of pure water and concentrated aqueous solutions of CsBr, RbBr, KBr, LiCl, $CaCl_2$, and $LaCl_3$ were measured at 25°C up to 2.5 kbars.

The NMR pulsed spectrometer was previously described (*14*). A high resolution Varian V-3800-1 15-inch electromagnet (air gap 3.8 inches) equipped with flux stabilizer and shim coils was used. The high pressure apparatus set-up will be described elsewhere (*15*). Atmospheric oxygen was removed by the freeze-pump-thaw technique. Samples were transferred from sealed degassing tubes into the high pressure sample cells in an oxygen-free argon atmosphere in a glove-box.

The samples were prepared from doubly distilled water. The compounds used are from the following sources: CsBr, A. D. Mackay, Inc. (chemically pure); RbBr, Alfa Inorganics, Inc. (optronic grade); KBr, Allied Chemicals (reagent grade); LiCl, Mallinckrodt Chemical Works (analytical reagent); $CaCl_2$, Mallinckrodt (analytical reagent); $LaCl_3$, Alfa Inorganics, Inc. (99.9%).

RESULTS AND DISCUSSION

The pressure dependences of the measured proton spin–lattice relaxation times T_1 of pure water and concentrated solutions of CsBr, RbBr, KBr, LiCl, $CaCl_2$, and $LaCl_3$ at concentrations of about 4.5 m are shown in Fig. 1. In order to better show the differences in the pressure dependences of individual electrolytes, the experimental data were also plotted as $T_1(P)/T_1(1)$, i.e., normalized to the values at atmospheric pressure.

Since the presence of Li^+, Ca^{++}, and La^{+++} in the aqueous solutions decreases the proton relaxation times relative to pure water, this implies a structure-making effect

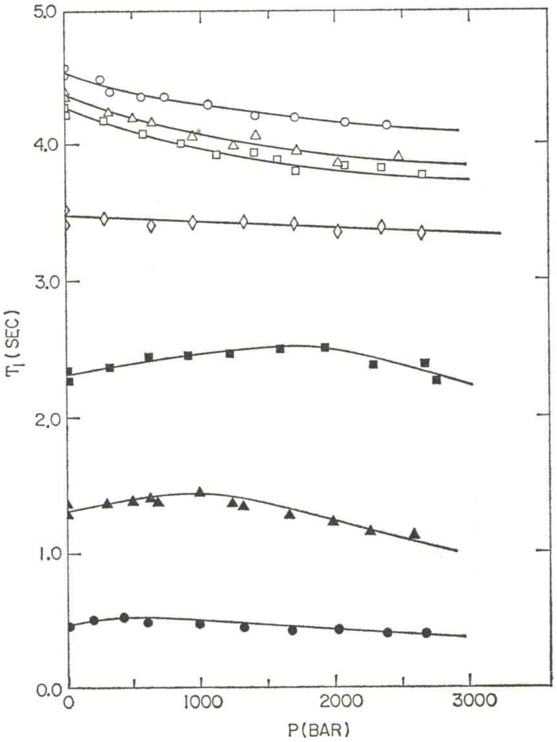

FIG. 1. The pressure dependence of the proton spin–lattice relaxation time T_1 in pure water and concentrated aqueous electrolytic solutions: ◇ pure water; ○ 4.4 m CsBr; △ 4.5 m RbBr; □ 4.5 m KBr; ■ 4.3 m LiCl; ▲ 4.5 m $CaCl_2$; and ● 4.5 m $LaCl_3$.

of these ions on water structure. On the contrary, K^+, Rb^+, and Cs^+ in the aqueous solutions increase the proton spin–lattice relaxation times of the water molecules, producing a structure-breaking effect. The present results are in agreement with those found by various other methods (*2*, *6*, *7*, *16*).

Bromide ions are only slightly structure-breaking and do not contribute significantly to the structure-breaking effects of Cs^+, Rb^+, and K^+. In aqueous solutions of LiCl,

TABLE 1

PROTON SPIN–LATTICE RELAXATION TIMES AT 25°C AND ATMOSPHERIC PRESSURE

Solution	T_1 from this study (sec)	T_1 given in Ref. (*17*) (sec)
Pure water	3.46	3.57
CsBr (4.4 m)	4.52	4.60
RbBr (4.5 m)	4.35	4.45
KBr (4.5 m)	4.26	4.26
LiCl (4.3 m)	2.29	2.27
$CaCl_2$ (4.5 m)	1.30	1.39
$LaCl_3$ (4.5 m)	0.47	—

$CaCl_2$, and $LaCl_3$, the slight structure-breaking effect of the chloride ions is insignificant (*11*) as compared to the strong structure-making effect of the small and/or highly charged cations. As a consequence, the discussions that follow are limited to only the structural influence of the cations on water. In Table 1, the proton spin–lattice relaxation times at atmospheric pressure from the present measurements are compared with those obtained by Endom, Hertz, Thul and Zeidler (*17*).

From Figs. 1 and 2 we see that the proton T_1 in pure water exhibits a very small pressure dependence. The proton relaxation mechanism of water molecules is mainly through dipole–dipole interactions, which can be separated into the intermolecular and intramolecular contributions. A general theory of the nuclear dipole–dipole relaxation mechanism has been developed by Bloembergen, Purcell, and Pound (*18*). With the application of Hubbard's equation (*19*) for the intermolecular dipole–dipole interactions and the Stoke–Einstein relation between viscosity and the self-diffusion constant, the equation relating the proton spin–lattice relaxation time T_1 to the motion of the water molecule is

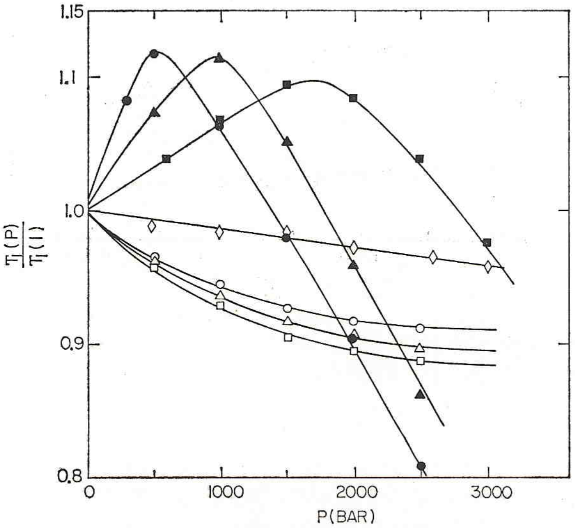

FIG. 2. The effect of pressure on the normalized proton $T_1(P)/T_1(1)$ at 25°C: ◇ Pure water; ○ 4.4 m CsBr; △ 4.5 m RbBr; □ 4.5 m KBr; ■ 4.3 m LiCl; ▲ 4.5 m $CaCl_2$; and ● 4.5 m $LaCl_3$

$$\frac{1}{T_1} = 2\pi\hbar^2\gamma^4 \frac{a^3}{r_{ij}^6}\frac{\eta}{kt} + \frac{6}{5}\pi^2 N\gamma^4\hbar^2 \frac{\eta}{kt} \times \left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 + \cdots\right], \quad [1]$$

where $\hbar$ is the Planck's constant divided by 2π, γ is the gyromagnetic ratio for hydrogen, r_{ij} is the hydrogen–hydrogen interatomic distance, a is the molecular radius of the water molecule, b is the distance of the proton from the center of the molecule, N is the number of spins per unit volume, and η is the viscosity in poise.

We calculated the proton spin–lattice relaxation times of pure water at 25°C and at different pressures, using Eq. [1]. The number of spins per unit volume N at various pressures was evaluated from Bridgman's data (*20*) on the pressure studies of the molar volume of liquid water. The viscosity of water up to 1.4 kbars was taken from the data of Stanley and Batten (*21*) while those at 2 and 2.5 kbars were from Bett and Cappi (*22*). Values for r_{ij}, a, and b were taken to be 1.52, 1.38, and 0.920 Å respectively. The calculated theoretical values of proton spin–lattice relaxation times of pure water and those from the present experimental measurements are given in Table 2.

TABLE 2

PRESSURE DEPENDENCE OF THE PROTON T_1 OF WATER AT 25°C

	Experimental		Calculated from Eq. [*1*]	
P (bars)	$T_1(P)$ (sec)	$T_1(P)/T_1(1)$	$T_1(P)$ (sec)	$T_1(P)/T_1(1)$
1	3.46	1.00	3.57	1.00
352	3.46	1.00	3.57	1.00
705	3.45	0.99	3.54	0.99
1055	3.43	0.99	3.50	0.98
1406	3.42	0.99	3.44	0.96
2000	3.40	0.98	3.36	0.94
2500	3.36	0.97	3.26	0.91

In view of the experimental errors in the measurements of η, N, and T_1, the agreement between the experimental and theoretical T_1 values can be regarded as excellent.

Both Figs. 1 and 2 show clearly the prominent difference betweeen the T_1-vs-pressure dependence for structure-breaking and structure-making electrolytes. Since the structure of water is broken to a great extent in the solution of a structure-breaking electrolyte, it is not surprising that the proton T_1 shows a dependence upon pressure analogous to a "normal" molecular liquid (*23, 24*). The pressure increase slows down the motion of the molecules, increasing the translational and reorientational correlation times and therefore increasing the proton spin–lattice relaxation rate. The normalized $T_1(P)/T_1(1)$ as given in Fig. 2 suggests that the relative change in T_1 with pressure follows the order of structure-breaking ability of the cations $Cs^+ > Rb^+ > K^+$.

A strikingly different behavior is exhibited by the proton T_1 in the solutions of structure-making electrolytes. In $LaCl_3$, $CaCl_2$, and LiCl solutions the initial application of pressure causes a decrease in the proton spin–lattice relaxation rate as the highly structured water is disrupted. The water molecules are then able to acquire more translational and rotational freedom. This is, of course, reflected in the change in T_1, which increases until a state is reached in which the water molecule has the greatest freedom to translate and rotate at a given temperature. This state corresponds to one of the maxima in the T_1-vs-p plots given in Figs. 1 and 2. After this maximum motional freedom is reached, further applied pressure will start to compress the "free" water molecules, resulting in an increase of dipolar interactions of the protons and therefore in an increase of proton relaxation rate. After the maximum, the T_1-vs-p plots show again a trend more typical for "normal" liquids. It is interesting to note that the relative locations of the maxima in the T_1-vs-p plots for $LaCl_3$, $CaCl_2$, and LiCl follow the order of the structure-making ability of the cations $La^{+++} > Ca^{++} > Li^+$. $LaCl_3$ solution exhibits a maximum at the lowest pressure when compared with the other two electrolytes.

One should try to discuss the data in terms of different structural models such as proposed, e.g., by Frank and Wen (*7*) or by Tikhomirov (*25*). But we feel that this discussion will necessarily be only tentative and somewhat ambiguous. At this point our understanding of the complex dynamic structure of concentrated aqueous electrolytes is far from satisfactory. Nevertheless, the experimental data show that the high pressure studies could help in elucidating some of the problems in the structure of aqueous solutions. Further work along these lines is underway in our laboratory.

ACKNOWLEDGMENTS

Our thanks are due to Professor H. G. Drickamer for bringing this problem to our attention.

REFERENCES

1. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, 1958.
2. O. Ya. Samoilov, "Structure of Aqueous Electrolyte Solutions and the Hydration of Ions," Consultants Bureau Enterprises, New York, 1965.
3. J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, San Francisco, 1964.
4. G. B. Benedek and E. M. Purcell, *J. Chem. Phys.* **22,** 2003 (1954).
5. H. G. Hertz and C. Radle, *Z. Phys. Chem.* (Frankfurt) **68,** 324 (1969).
6. G. J. Safford, P. S. Leung, A. W. Naumann, and P. S. Schaffer, *J. Chem. Phys.* **50,** 4444 (1969).
7. H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.* **24,** 133 (1957).
8. R. A. Horne, *Nature* **200,** 418 (1963).
9. R. A. Horne and D. S. Johnson, *J. Phys. Chem.* **70,** 2182 (1966).
10. R. A. Horne and R. P. Young, *J. Phys. Chem.* **71,** 3824 (1967).
11. P. S. Leung and G. J. Safford, *J. Chem. Phys.* **74,** 3696 (1970).
12. Y. Lee and J. Jonas, unpublished results.
13. D. Eisenberg and W. Kauzman, "The Structure and Properties of Water," p. 223, Oxford University Press, New York, 1969.
14. J. Jonas, T. E. Bull, and C. A. Eckert, *Rev. Sci. Instr.* **41,** 1240 (1970).
15. J. Jonas, unpublished data.
16. H. G. Hertz, "Progress in Nuclear Magnetic Resonance Spectroscopy" (J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Eds.), Vol. 3, p. 159, Pergamon Press, Oxford, 1967.
17. L. Endom, H. G. Hertz, B. Thul, and M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.* **71,** 1008 (1967).
18. N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73,** 679 (1948).
19. P. S. Hubbard, *Phys. Rev.* **131,** 275 (1963).
20. P. W. Bridgman, *J. Chem. Phys.* **3,** 597 (1935).
21. E. M. Stanley and R. C. Batten, *J. Phys. Chem.* **73,** 1187 (1969).
22. K. E. Bett and J. B. Cappi, *Nature* **207,** 620 (1965).
23. T. E. Bull and J. Jonas, *J. Chem. Phys.* **52,** 4553 (1970).
24. T. E. Bull and J. Jonas, *J. Chem. Phys.* **53,** 3315 (1970).
25. V. I. Tikhomirov, *J. Struct. Chem.* **4,** 479 (1963).

PRINTED IN GREAT BRITAIN BY THE WHITEFRIARS PRESS LTD, LONDON AND TONBRIDGE.